# AN ASSESSMENT OF PRODUCED WATER IMPACTS IN THE GALVESTON BAY SYSTEM

by

R.W. Roach, R.S. Carr, C.L. Howard, and B.W. Cain

1993

AN ASSESSMENT OF PRODUCED WATER IMPACTS IN THE GALVESTON BAY SYSTEM

by

R.W. Roach[sup]1, R.S. Carrý, C.L. Howard[sup]3, and B.W. Cain[sup]1

ÄÄÄÄÄÄÄÄÄÄÄÄÄÄÄÄÄÄÄÄÄÄÄÄÄÄÄÄ
[sup]1 U.S. Fish and Wildlife Service, Division of Ecological Services, 17629 El Camino Real #211, Houston, TX 77058

ýU.S. Fish and Wildlife Service, NFCR Field Research Station, CCSU, Campus Box 315, 6300 Ocean Drive, Corpus Christi, TX 78418

[sup]3 University of Houston-Clear Lake, Biology Department, 2700 Bay Area Blvd., Houston, TX 77058

## EXECUTIVE SUMMARY

Texas Railroad Commission (TRC) 1991 data indicated that the Galveston Bay system and its tributaries were permitted to receive up to 363,000 barrels (15.2 million gallons) of produced waters per day from 93 permitted sources. This data provided only a very gross estimate (probably overestimates) of actual discharge volumes because they are based on annual tests of well potential rather than actual flow rates. Produced waters typically contain high levels of dissolved solids ranging in salinity from 12 to 180 parts per thousand, metals concentrations higher than those of receiving waters, radium-226, and soluble and dispersed hydrocarbons. The TRC issues tidal disposal permits, provided that the discharge meets applicable Texas Surface Water Quality Standards. The Environmental Protection Agency (EPA) currently does not regulate these discharges under its National Pollutant Discharge Elimination System (NPDES).

Impacts to wetland vegetation are the most obvious signs of environmental effects resulting from brine spills or discharges. Emergent marsh plants such as smooth cordgrass and gulf cordgrass

are easily killed, even by small volume or intermittent discharges. These "burned" marsh areas are the result of sodium accumulation in soils and may take years to revegetate. Produced water effects on unvegetated areas (bayous, bay margins, and open bay) are not as apparent, but possibly as severe.

Recent studies of the effects of brine upon estuarine systems have shown that: 1) high levels of dissolved solids allow the formation of a density gradient, especially in low energy systems such as bayous; 2) oil and chlorides are incorporated into sediments near discharges, severely depressing the abundance and richness of benthic infauna; 3) elevated salinities inhibit nekton movement; 4) petroleum hydrocarbons are ingested and incorporated into the tissues of various aquatic organisms: and 5) these effluents and nearby sediments are highly toxic to a wide variety of estuarine organisms.

This study provides a general assessment of any adverse environmental effects resulting from tidal disposal of produced waters by: 1) documenting any alterations to the benthic macroinvertebrate communities; 2) physically and chemically characterizing impacted and unimpacted sediments; and 3) assessing the sediment toxicity caused by these discharges.

The Tabbs Bay site (a shoreline discharge) and the Cow Bayou site were the primary study sites selected for characterization within the Galveston Bay system due to their high discharge volumes. Transects were established radiating from the discharge into Tabbs Bay. Four stations in Cow Bayou and 2 stations in Robinson

Bayou (a reference bayou also influenced by urban runoff) were selected to assess impacts upon bayou habitats.

Sediment samples were collected for residue analyses of organic and inorganic constituents using a 4-inch diameter coring device. Total organic carbon, acid volatile sulfides and grain size analyses were also conducted.

A suite of bioassays were conducted using sediment interstitial water samples (pore waters) and resuspended and solid-phase sediment bioassays. These tests were conducted using sea urchins (Arbacia punctulata), burrowing amphipods (Grandidierella japonica) and (Hyallela azteca), and the grass shrimp (Palaemonetes pugio).

Five replicate core samples were collected at each station for macroinvertebrate identification and enumeration using a modified Mackin 2-inch coring device. These samples were preserved, sieved with a No. 60 mesh screen and stained for identification.

Striped mullet were collected from discharge-impacted (Tabbs Bay and Cow Bayou) and reference sites (Christmas Bay and Robinson Bayou) for analysis of bile polycyclic aromatic hydrocarbon (PAH) metabolites as indicators of exposure to PAHs in the water column.

In Cow Bayou benthic macroinvertebrates ranged in abundance from 0/mý at the station nearest the discharge to 5,314/mý at the mouth

of the bayou. By comparison, benthos numbered 14,760/mý in Robinson Bayou. Abundance, species richness, and diversity followed the same pattern: Cow Bayou stations differed significantly or greatly from Robinson Bayou stations. The degree of biological impairment was inversely proportional to the distance from the discharge. Petroleum hydrocarbons and strontium in the sediments collected were highest in samples collected from the discharge ditch (oil and grease = 55,900 ppm) and gradually decreased with distance to background levels. Solid-phase bioassays conducted with grass shrimp using sediments from Cow Bayou showed significant toxicity only at the station nearest the discharge; however, benthic communities and sediment chemistry analyses revealed a greater degree of impact for the entire length (approximately 3400 feet) of Cow Bayou.

In Tabbs Bay, the center transect showed significantly reduced abundance, richness and diversity out to 270 feet from the discharge (the next station was 1,200 feet from the discharge). Sediment and pore-water toxicity data indicated significant impact within 1,200 feet of the Tabbs Bay discharge. Sediment interstitial water, or pore water, collected for toxicity testing had increased salinity and ammonia concentrations at stations near the discharge. Barium and strontium in sediment was highest



at the station nearest the discharge and gradually diminished to background levels at the furthest stations, clearly indicating the source of the contaminants was the discharge. Analyses for petroleum hydrocarbons again showed this same pattern. Metabolites of the PAHs naphthalene, phenanthrene, and benzo[a]pyrene were quantified in composite striped mullet bile samples. The two brine-influenced sites, Tabbs Bay and Cow Bayou, had considerably higher concentrations of each metabolite than their respective reference sites. Metabolites in samples collected from Tabbs Bay were an order of magnitude higher than in samples collected from nearby Morgan's Point, as part of another study.

The independent results of benthic community analyses, sediment chemistry analyses, and sediment and pore-water toxicity tests clearly show that produced water discharges contaminate sediments near them to the extent that infauna are absent or only minimally colonizing them. The most important factor governing the magnitude and extent of contamination or biological impairment caused by any discharge is the degree to which it is mixed into the receiving water body. Discharges to the open Gulf and open bay are better mixed by tidal currents and water depth than discharges to slow-moving bayous and protected shorelines. Bayous and shorelines receive a large proportion of brines discharged in the Galveston Bay system and they are typically more important habitats to fish and wildlife resources. Because of their poor mixing, a greater potential for impact can be expected. Future management of this type of discharge should include a detailed site assessment and recommendations to eliminate or minimize environmental degradation.

Historically the TRC did not require reporting of actual discharge volumes, water quality parameters other than oil and

grease concentration, or exact discharge location, making accurate impact assessments impossible. The TRC is currently updating their permit files and has included additional reporting and monitoring requirements. In doing so, the TRC now has an accurate estimate of tidal disposal discharges and the volumes discharged into Galveston Bay. Recent estimates of the number of active dischargers, not just permittees, puts the figure at approximately 62 (and a more accurate estimate of 137,000 bbls per day) in the Galveston Bay system. Of the newly estimated 137,000 bbls per day, approximately 80,000 bbls are from one source, which will voluntarily begin deep-well injection in early 1993.

Although the EPA does not currently regulate these discharges under its NPDES program, they are drafting general NPDES permits for each of the five discharge subcategories. The ones of concern for the Galveston Bay system, the Coastal and Stripper subcategories, soon will be issued as a proposed rule, open for public comment. As currently drafted, this proposed rule will



require "no discharge" to marshes, wetlands, swamps, bayous or coastal bays from all wells, including stripper wells. The Onshore Subcategory, which has a similar no discharge limitation (except for stripper wells) became a final rule March 27, 1991.



TABLE OF CONTENTS

FIGURES





TABLES

## ACKNOWLEDGMENTS

We owe thanks to many individuals for their assistance with this study. Dede Albe provided invaluable assistance throughout every phase of the study. Dede assisted us in the field, in the lab by preparing the samples and catalogs for shipping, and by skillfully organizing and managing the data. Her efforts contributed greatly to the completion of this report. Duane Chapman assisted in the collection of field samples and spent many hours conducting several of the bioassays. We appreciate the helpful comments of many reviewers. Finally, we thank Janice Santafede, Wendy Isaacson, and Elaine Schaffer for typing this report. This study was funded in part by the U. S. Fish and Wildlife Service, Division of Refuges.



## INTRODUCTION

In the process of recovering oil and gas, water is also withdrawn from underground geological formations. The American Petroleum Institute estimates that approximately nine barrels (bbls) of water are recovered for each barrel of oil. This water-oil mixture is usually separated by flotation or gravity separation in tank batteries, heat separation, use of simple skimming pits, or some combination of these. The remaining water, sometimes called produced water or oilfield brine, is then either deep-well injected, or discharged to surface waters, as permitted.

Produced waters typically contain high levels of dissolved salts, with salinities ranging from 20 to 180 parts per thousand (ppt), elevated concentrations of trace metals, and up to 25 parts per million (ppm) petroleum hydrocarbons (Harper 1986). High concentrations of radium-226 may also be prevalent in produced waters. Concentrations of radium-226 in brines often exceed regulatory criteria established for other industries (Reid 1983).

Brines are often disposed via deep-well injection back into the underground formation from which they were withdrawn to enhance oil and gas recovery. A common method of brine disposal along the Texas coast is discharge to surface waters, either directly or by overland flow. Brines discharged into freshwater streams have caused such obvious water quality problems, including fish kills, that they are currently restricted to tidal reaches of the gulf. This disposal method, known as "tidal disposal", is restricted to tidally influenced water bodies within Texas.

In Texas the Railroad Commission (TRC) regulates all activities pertaining to oil and gas production, including the disposal of wastes. The TRC issues tidal disposal permits, provided that the effluent meets applicable Texas Surface Water Quality Standards and averages less than 25 ppm oil and grease. The Environmental Protection Agency (EPA) does not currently regulate these discharges under its National Pollutant Discharge Elimination System (NPDES) program. EPA has issued or is proposing NPDES permits for different discharge subcategories - including stripper, coastal, and onshore. Stripper wells are defined as those producing less than 10 bbls of oil per day.

TRC estimates indicate that the Galveston Bay System and its tributaries were permitted to receive more than 326,000 bbls of produced waters per day from 92 sources in 1989, and more than 363,000 bbls per day in 1990 (Figure 1). This same data also suggests that fifty-seven percent of the discharges (by estimated

See Table/Figure

Figure 1. Locations of produced water discharges in the Galveston Bay System (modified from TRC 1991 data).



volume) went to bayou systems; shoreline and open-bay discharges accounted for 35 and 8 percent, respectively. For comparison, total daily discharge estimates are 740,000 bbls in Texas to 2,000,000 bbls in Louisiana. Caution must be used in interpreting this data, because it is based on annual tests of well potential, not actual flow data (TRC, personal communication). Actual flows vary with current production rates and the age of the reservoir. Older fields yield increasingly more water. The TRC does not require dischargers to report or estimate actual flow rates in their monitoring reports. These discharges are continuous, ceasing only when oil:water ratios make it economically infeasible to continue production.

The chronic exposure of estuarine habitat to oil pollution is potentially more damaging than accidental oil spills. Estuaries provide valuable nursery habitat for commercially and recreationally important aquatic species. They are also productive sources of food for these fish and shellfish as well as many migrant shorebird, fish-eating bird and waterfowl species. There is little documentation regarding the degradation of these habitats caused by produced waters and possible uptake of petroleum and heavy metals by fish and wildlife inhabiting these areas (USFWS 1986).

A review of available literature indicates that the effects commonly associated with these discharges are contamination of nearby sediments and degradation of bay bottom habitats. These studies differ among each other regarding the areal extent and degree of contamination, making assessments on a larger scale difficult. Further, the TRC does not accurately monitor actual discharge volumes, oil concentration, or exact discharge location, determining accurate impacts is impossible. Thus, because of obvious impacts to vegetation and intermittent streams, documentation of some localized impacts, and a lack of information and regulation regarding permitted discharge volumes and their locations, there are growing concerns of potential degradation of coastal habitats caused by produced water discharges.

The most important factor governing the degree of contamination or biological impairment caused by any produced water discharge is the extent to which it is mixed by the surrounding water body (Harper 1986). Figure 2 shows an estimated distribution of produced water discharges to the Galveston Bay, Texas system by three categories, representing different mixing regimes: 1) tidal bayous or other restricted bodies of water; 2) shorelines of open bays; and 3) open bay discharges. A fourth category, open gulf discharges, is not included because many previous studies adequately describe their impacts. Also, open Gulf discharges present much less potential threat to fish and wildlife resources because of their relatively small number, low volumes, and good mixing. Armstrong et al. (1979) has



See Table/Figure

Figure 2. Estimates or produced waters discharged to different environments in the Galveston Bay System.

See Table/Figure

Figure 3. Location of Cow Bayou and Tabbs Bay study sites.



characterized brine discharges in the third category, open bay habitats, concluding that they produce a relatively restricted (150 m radius) zone of effect. Second to gulf discharges, open

bay discharges are generally better mixed by tidal currents and water depth than discharges to bayous and along shoreline areas.

The purpose of this study is to describe the nature and extent of contamination resulting from produced water discharges to bayous and shorelines for the following reasons: 1) they receive a large proportion of brines discharged in the Galveston Bay System; 2) they are typically more important habitats to fish and wildlife resources; and 3) because of poor mixing, a greater potential for impact can be expected.

In addition to the two primary study sites, other samples were collected from discharges in the center of Trinity Bay, on the east shoreline of Trinity Bay, on Anahuac National Wildlife Refuge, in the Intracoastal Waterway near High Island, and in Nueces Bay, and are included in this assessment (Table II-10). The study objectives were to: 1) physically and chemically characterize brine-impacted and unimpacted sediments; 2) document any associated to the benthic macroinvertebrate communities; and 3) to assess the toxicity caused by these discharges.



## METHODS

Because brines contain high concentrations of dissolved solids, they settle to the bottom of the water column and into the sediments, allowing petroleum and heavy metals to absorb to and contaminate these sediments to a much greater degree than other wastewater discharges. A useful approach for determining the source or degree of biological impairment in sediments is the sediment quality triad (Chapman et al. 1991). As such, this study focused on sediment quality and the SQT approach to characterize impacts near brine discharges.

This approach combines the more traditional bulk sediment analyses with a measure of in situ effects, i.e. benthic community parameters, and sediment and pore-water toxicity tests, as per the sediment quality triad approach. In addition to these sediment samples, limited samples of tissues, as well as effluent, water column, and surface microlayer samples were also collected.

### STUDY SITES

The two primary study sites, Cow Bayou and Tabbs Bay (Figure 3), were selected because of the large volume of discharges they receive, making any impacts easier to detect (Harper 1986). These two sites represent different mixing regimes - Cow Bayou is a brackish bayou influenced by urban and storm runoff, whereas the Tabbs Bay site is an open-bay shoreline discharge affected by wave action and tidal currents.

Because of extensive urban development in the Cow Bayou watershed, runoff from rainfall is very high. This tends to resuspend and scour the sediments periodically, and makes Cow Bayou less typical of natural or normal bayous whose flushing rates are much lower. Four stations in Cow Bayou and two stations in Robinson Bayou (a nearby reference bayou influenced

by urban runoff from League City) were selected to assess the brine discharge impacts to bayou habitats (Figure 4). In Tabbs Bay, three transects were established radiating from the discharge point out into Tabbs Bay (Figure 5). A reference site was located approximately four miles away in upper Galveston Bay.



See Table/Figure

Figure 4. Cow Bayou study site, Harris County, Texas.



See Table/Figure

Figure 5. Tabbs Bay study site, Harris County, Texas.



## SAMPLE COLLECTION

### Benthic macroinvertebrates

Seven replicate sediment samples were collected at each station using a modified Mackin 2-inch coring device with a clear Lexan cylinder (Baker, et al. 1977). These samples were examined for the presence of an oxidized sediment surface, evidence that the sample had been collected evenly and without disturbance. Only undisturbed samples were retained for analysis.

In the field, each sample was placed in a plastic container and preserved with 10% buffered formalin. Once in the laboratory, the sample number and dates collected, received, and processed were recorded in the sample log book. Each sample was then washed gently through a #60 (0.25 mm) mesh sieve to remove the sediment. All material remaining on the screen was washed into a wide-mouth plastic container, represerved with 10% buffered formalin, and stained with a mixture Eosin B and Sudan IV dyes. Each sample was labeled with the station number, replicate number, and date collected.

### Sediment Chemistry

Additional sediment samples were collected from these same stations for chemical analysis and toxicity tests using a 4-inch diameter PVC coring device. Analytical methodologies are described in Appendix I. Again, all samples were examined for the presence of the light brown oxidized surface layer before being included in the composite sample. Sediment samples (each approximately 10-15 cm in depth) from one station were pooled in a large stainless steel bowl and homogenized using a stainless steel spoon (approximately 5-liter total volume). Aliquots of this composite sample were then placed in 1-Chem chemically cleaned glass jars, labeled, placed on ice, then were frozen and shipped to USFWS contract laboratories for trace metal scans, GC/MS quantification of petroleum hydrocarbons, radium, acid

volatile sulfides, total organic carbon, and grain size analyses (Appendix II, Table II-1). Table II-2 gives the estimated limits of detection for various analyses and matrices.

Sediment Toxicity

The composite sediments described above were also used for toxicity testing. Subsamples were transferred to Ziploc[sup](R) plastic bags and kept on blue ice in the field. These sediment samples were used in solid-phase tests with amphipods and grass shrimp, and pore water toxicity tests.

The pore water was extracted within two days after the samples were collected using pressurized squeeze extraction devices with polyethylene filters (5 æm pore size). The pore water was frozen



immediately after it was extracted and stored frozen until the day before the start of the toxicity test, at which time the samples were thawed at room temperature or in a warm water bath. Water quality measurements (dissolved oxygen, pH, temperature and ammonia) were recorded and the salinity of the samples adjusted to 30ñ1 ø/ì, if necessary, using milli-Q deionized water or hypersaline brine. Sediment pore-water samples were used in Arbacia tests. Additional sediment was collected for palaemonetes toxicity tests.

Surface microlayer samples were collected with a device comprised of a hydrophobic Teflon[sup]R plate and squeegees (Carr and Chapman 1992). This device is a modification of the collection apparatus described by Hardy et al. (1985). Surface microlayer samples were placed on blue ice immediately, frozen within 12 hours after collection, and stored frozen until just prior to testing.

TOXICITY TESTS

Several different bioassays were conducted using sediment, pore waters, surface microlayer samples, and effluents from the Tabbs Bay stations. Solid-phase and resuspended sediment bioassays were conducted using sediments from selected stations at Tabbs Bay and Cow Bayou (Table II-3).

Solid-phase Testing

Grandidierella japonica. The toxicity of the sediments from stations located on the Tabbs Bay central transect, the Galveston Bay reference site, and an additional control was determined using a static 10-day solid-phase test (ASTM 1990) with the corophiid amphipod G. japonica. Sediment samples were held on ice or refrigerated during transport and storage. The test was started within one week of sample collection, and was conducted under static conditions in environmental chambers at 20øC, 30ñ1 ø/ì salinity and a 14:10 light:dark cycle. One liter 1-Chem[sup](R) glass jars with Teflon[sup](R)-lined lids were used for exposure chambers. Gentle aeration was supplied to each exposure chamber to ensure that dissolved oxygen levels remained above 80% saturation. Water quality measurements (temperature, dissolved oxygen, salinity, pH, ammonia) were made on each exposure chamber

at the beginning, day 4, and at the termination of the 10-day exposure. G. japonica were obtained from in-house laboratory cultures that have been cultured a minimum of three generations. The animals were retrieved from the culture aquaria with a fine mesh net on the day of the start of the test. Only non-gravid animals larger than 2.5 mm were included. The animals were randomly transferred individually to 20 ml vials and the vials randomly selected for addition to the test chambers. A reference sediment was also tested in conjunction with the test sediments.



Hyallela azteca. Solid phase bioassays were conducted with sediments from stations TB01-4 and the reference, GBR, using the amphipods H. azteca in 28-day test and G. japonica in a 7-day test.

Palaemonetes pugio. The grass shrimp, P. pugio, was used in resuspended and whole sediment bioassays. At selected stations within both of these study sites (CB01, CB04 in Cow Bayou, RB01, RB02 in Robinson Bayou, stations TBO1-TBO4 in Tabbs Bay and GBR) additional sediment was collected for these bioassays. These tests were conducted according to the Draft Ecological Evaluation of Proposed Discharge of Dredged Material into Ocean Waters (EPA-503-8-91/001 1991) procedures for Tier III bioassays (96-hour resuspended sediment and 10-day benthic tests)

Pore-water Toxicity Testing

The toxicity of the sediment pore water and positive control samples was determined using two different tests with the sea urchin Arbacia punctulata. The toxicity tests conducted in this study were the sperm cell test and the morphological development assay (Carr and Chapman 1992). Each of these tests utilizes different end points, thereby providing different information regarding the mode of toxicity of the sediment-associated contaminants. A dilution series test with sodium dodecyl sulphate was also conducted with each sperm cell test series as a positive control and the EC50 determined in order to maintain a record of gamete viability and test acceptability.

In addition to the tests with sea urchins, the toxicity of sediment pore water and surface microlayer, and water column samples from Tabbs Bay to embryo/larval stages of red drum was determined. The static 48-hour tests were commenced with newly fertilized embryos at 25øC, 37ñ2 ø/[sub]00 salinity, and 14:10 hour light:dark cycle in an environmental chamber according to American Society for Testing and Materials (ASTM 1988) procedures. The exposure chambers were glass Stender dishes with ground glass lids with 10 ml of exposure media and 5 embryos per dish and 5 replicates per treatment. Water quality measurements were made at the beginning and at the termination of the test.

All manipulations and sample transfers were recorded on standardized data sheets. A reference pore water sample collected from Redfish Bay, Nueces County, Texas, which was handled identically to the Galveston Bay samples, was included with each series of pore-water toxicity tests as a negative control. This reference site is far removed from any known

sources of contamination and has been used previously as reference site (Carr and Chapman 1992). Millipore filtered (0.45 jim) seawater and reconstituted brine (30 ø/[sub]00 salinity) controls were included with every series of tests.



Other

Grass shrimp surviving exposure from the toxicity tests were analyzed for induction and accumulation of contaminant-specific stress proteins. Striped mullet were collected from discharge-impacted (Tabbs Bay and Cow Bayou) and reference sites (Christmas Bay and Robinson Bayou) for analysis of polycyclic aromatic hydrocarbon (PAH) metabolites in bile, indicators of exposure to PAHs in the water column. Each fish's total weight, liver weight, length, sex, and any gross abnormalities were recorded. Individual bile samples were collected in vacutainers. Each tube was labeled, weighed and frozen for analysis of bile metabolites of PAHs. They were composited at the laboratory by mixing equal aliquots from each vacutainer by location. These samples were sent to a USFWS contract laboratory for determination of PAH metabolites



## RESULTS

COW BAYOU

Benthic communities are often used as pollution monitoring tools. Community parameters such as abundance, richness, and diversity are easily affected by pollution from various sources. In Cow Bayou, the sampling station at its confluence with Clear Creek was divided into upstream and downstream stations (CB04u and CB04d) for the collection of benthos only. This was done to further assess any effects attributable to hydrology.

Benthic macroinvertebrates ranged in number from 0/mý at the station nearest the discharge to 5,314/mý at CB04u. In comparison there were 14,760/mý in Robinson Bayou, the reference site. The average number of species identified per station ranged from 0 to 6.4. Diversity, as calculated by the Shannon-Weaver function,

See Table/Figure

ranged from 0 nearest the discharge to 1.43 at the reference station, RB02. A Hartley's F-test indicated non-normal distribution of variance for the parameter abundance or total number of individuals; therefore, abundance was log(x+1) transformed prior to analysis of variance (ANOVA). The number of species, or richness, and diversity were not transformed for this study site. Log-transformed abundance differed significantly (rý=0.65, p<0.0001) between sample stations; however, Duncan's multiple range test (SAS 1988) showed significant mean differences (df=34, à=0.05) only for stations CB01, CB02, and CB03 versus the reference. Figure 6 shows an apparent (but not

statistical) difference in abundance between both CB04u and CB04d, and the reference stations RB01 and RB02. Richness differed between stations (rý-0.80, p<0.0001) with the means of all stations differing significantly from the reference station RB02 (Figure 6). The diversity index H' followed the same pattern: stations were significantly different (rý=0.77, p<0.0001) and stations RB01, RB02 and CB04u (the upstream confluence station) had significantly greater mean diversities than all other stations (Figure 6).

The aromatic and aliphatic hydrocarbon results reported for sediments (Table II-4) were summed by sample station and are presented with the oil and grease analyses in Figure 7. Results



See Table/Figure

Figure 6. Abundance, richness, and diversity of benthic macro-invertebrates in Cow Bayou, Harris County, Texas. (* denotes significant difference from reference station)



See Table/Figure

Figure 7. Sediment contaminants in Cow Bayou, Harris County, Texas.



of the trace metals analyses are shown in Table II-5. Of special interest are barium and strontium, as they are markers of brine discharges. St. Pe' (1990) and Boesch and Rabalais (1989b) described a similar pattern in Louisiana. In stable salinity regimes, both barium and strontium precipitate from the water column. Where salinity is more variable, such as tidal bayous, only strontium is found elevated in sediments. The results of our study agreed (Figure 7)

The results for radium-226 analyses for both water and sediment samples are presented in Table II-9. Although radium-226 in produced waters may greatly exceed standards set for other industries, radium and all other oil production wastes were exempt from Resource Conservation and Recovery Act regulations (Shipley 1988). These results offer little as to the interpretation of possible ecological effects in this study, and therefore are not discussed further.

Solid-phase bioassays conducted with grass shrimp using sediments from Cow Bayou and Robinson Bayou showed significant toxicity only at the nearest station, CB01 (survival=70%). Resuspended sediment bioassays showed no significant impact at any station.

TABBS BAY

The Tabbs Bay site was sampled more intensively, but the results are more difficult to interpret. The effect of tidal currents on

the discharge plume are shown in the differing results for each sample station. Data for benthic communities' abundance, richness and diversity were log(x+1) transformed prior to ANOVA analyses. Differences between stations were significant for each log transformed parameter (rý=0.62, p<0.0001 for abundance, rý=0.70, p<0.0001 for richness, rý=0.70, p<0.0001 for diversity). The center transect, stations TB01-TB04, showed significantly reduced abundance, richness, and diversity (Figure 8) at stations TB01 and TB02, nearest the discharge (log transformed data, Duncan's multiple range test df=31, à=0.05).

The pattern seen in benthic community parameters is repeated in the sediment contaminants samples (Figure 9). samples from the east transect, stations TB01, TB05 and TB06, indicate only the closest station, TB01, to be significantly affected by the discharge (Table II-6). TB05 and TB06 are approximately the same distance from the discharge as are TB03 and TB04, respectively (Figure 5). The west transect, stations TB07, TB08 and TB09, showed the same results. Two additional stations, TB11 and TB12, were located nearshore, approximately 150 yards west and east of the discharge point, to further define the plume. While these stations differed significantly from each other, only diversity (H') at TB11 was significantly reduced relative to the reference,



See Table/Figure

Figure 8. Abundance, richness, and diversity of benthic macro-invertebrates in Tabbs Bay, Harris County, Texas. (* denotes significant difference from reference station)



See Table/Figure

Figure 9. Sediment contaminants in Tabbs Bay, Harris County, Texas.



GBR. This was likely due a westward drift of the discharge plume.

Further evidence of the plume's slight westward drift is found in the sediment chemistry. Barium, strontium, oil and grease, summed aliphatics, and summed PAHs all decreased with distance from the outfall (Table 1). Table 1 shows that the west transect was consistently higher in all of these values relative to the other two transects. The shoreline transect also illustrates this east to west drift.

TOXICITY TESTS

Sediment interstitial water, or pore water, collected for toxicity testing, had increased salinity and ammonia concentrations at stations near the discharge (Figure 10).

Acute toxicity tests, using larval red drum, did not show significant toxicity in relation to the distance from discharge. In fact red drum responded in a pattern opposite of all other tests, due to their sensitivity to unionized ammonia concentrations (Carr, unpublished data). A. punctulata pore water bioassays conducted using the methods described by Hose (1985) demonstrated patterns reflective of those shown by the benthic community structure (Figure 8) and sediment chemistry data (Figure 9). Solid-phase toxicity tests using infaunal amphipods, H. azteca (Burch, unpublished data) and G. japonica again illustrate this same pattern (Figure 10).

Grass shrimp surviving the resuspended sediment and solid-phase bioassays from both Tabbs Bay and Cow Bayou were analyzed for the induction of stress proteins. Stress proteins were identified by gel electrophoresis and quantified by scanning densitometry. Although significant lethality occurred only with sediments from station TB01 in these tests, grass shrimp significantly accumulated two stress proteins at stations nearest the discharges (Howard, unpublished data). Although the effects of these biochemical changes at the population level are unknown, they reflect the gradients seen in benthic community structure, sediment chemistry, and more sensitive toxicity tests.

Biliary metabolites of the PAHs naphthalene, phenanthrene, and benzo[a]pyrene were quantified for five composite striped mullet samples. The two brine-influenced sites, Tabbs Bay and Cow Bayou, had considerably higher concentrations of each metabolite than their respective reference sites (Table 2). Metabolites in samples collected from Tabbs Bay were an order of magnitude higher than in samples collected from nearby Morgan's Point, as part of another study. These results represent composited samples, not averages, therefore no statistical comparisons were made.



Table 1. Sediment content of barium, strontium, oil and grease, äPAHs, and äaliphatics in Tabbs Bay, by transect.

| Transect | Station | BA[sup]1 | SR[sup]1 | OILý | äPAHý | äALIý |
|---|---|---|---|---|---|---|
| East | TB0l | 1240 | 599.0 | 1930 | 0.35 | 4.810 |
| | TB07 | 549 | 93.6 | 810 | 0.21 | 0.810 |
| | TB08 | 235 | 48.7 | 620 | 0.15 | 0.450 |
| | TB09 | 131 | 37.6 | 422 | 0.08 | 0.320 |
| | GBR | 128 | 26.8 | 290 | 0.03 | 0.210 |
| Center | TB01 | 1240 | 599.0 | 1930 | 0.35 | 4.810 |
| | TB02 | 836 | 478.0 | 3630 | 0.36 | 6.940 |

| | | | | | |
|---|---|---|---|---|---|
| | TB03 | 626 | 104.0 | 686 | 0.26 |
| 0.710 | | | | | |
| | TB04 | 206 | 44.5 | 566 | 0.26 |
| 0.600 | | | | | |
| West | TB01 | 1240 | 599.0 | 1930 | 0.35 |
| 4.810 | | | | | |
| | TB05 | 671 | 97.4 | 814 | 0.34 |
| 1.200 | | | | | |
| | TB06 | 398 | 55.9 | 762 | 0.53 |
| 0.980 | | | | | |
| Shoreline | TB11 | 4560 | 386.0 | 1150 | 0.29 |
| 1.430 | | | | | |
| | TB01 | 1240 | 599.0 | 1930 | 0.35 |
| 4.810 | | | | | |
| | TB12 | 104 | 13.5 | 240 | 0.01 |
| 0.230 | | | | | |

[sup]1 mg/kg dry weight

ý ppm wet weight



Table 2. PAH metabolites in striped mullet bile collected from five sites in the Galveston Bay System.

| | | Metabolite (ng/g, wet weight) | | |
|---|---|---|---|---|
| Location | n | napthalene | phenanthrene | benzo[a]pyrene |
| Tabbs Bay | 5 | 1,700,000 | 210,000 | 1,000 |
| Morgans Point[sup]1 | 2 | 150,000 | 35,000 | 425 |
| Christmas Bay | 7 | 100,000 | 20,000 | 550 |
| Cow Bayou | 7 | 280,000 | 50,000 | 680 |
| Robinson Bayou | 2 | 150,000 | 23,000 | 390 |
| Robinson Bayou | 2 | 110,000 | 25,000 | 330 |

[sup]1 Sue McDonald, pers. comm.



See Table/Figure

Figure 10. Pore water salinity and ammonia, and solid-phase and porewater toxicity tests using Tabbs Bay sediment.
(* denotes significant toxicity)



## DISCUSSION & CONCLUSIONS

Recent studies (Boesch and Rabalais 1989a, Boesch and Rabalais 1989b, St. Pe' 1990, Rabalais et al. 1991) on the effects of

brines discharged to estuarine systems in Louisiana have shown that: (1) high levels of dissolved solids allow the formation of a density gradient, especially in low energy systems such as bayous; (2) oil and chlorides are incorporated into sediments near discharges, severely depressing the abundance and richness of benthic infauna; (3) and petroleum hydrocarbons and radium are ingested and incorporated into the tissues of various organisms.

The effects of produced water discharges into estuarine habitats are documented in this study by: (1) absence of or significant effects on benthic communities; (2) significant toxicity of sediments and pore water; (3) elevated contaminant loadings in sediment; and (4) high biliary concentration of PAH metabolites in fish. Figures 6, 7, and a show that benthic and macroinvertebrate communities are absent or reduced in all of Cow Bayou as compared to a similar brackish bayou. In Tabbs Bay, benthos were significantly impacted in only the two closest sampling stations perpendicular to the shoreline (270 feet) and near the shoreline to the west (450 feet). The next tier of stations, located approximately 1,200 feet away did not differ significantly in benthos from the reference site in upper Galveston Bay. Assuming that the discharge forms a round plume, estimates of the zone of impact range from 1.3 acres (diameter = 270 feet) to 5.25 acres (radius = 270 feet). Armstrong et al. (1979) and Mackin (1973) described similar areas of impact resulting from other discharges in Galveston Bay. Three separate bioassays showed significant toxicity at the first two stations in Tabbs Bay, with only two species showing a significant response at station TB03. Pore water salinities and ammonia concentrations also show this graded effect with station TB03 still having higher concentrations than background. More sample stations would be needed in the 300-1,200 feet range to better define the extent of the biological or toxicological impact zone.

Sediment chemistry data from Tabbs Bay show a much more rapid drop from source to outer sampling station in concentrations of barium, strontium, oil and grease, aliphatic and PAHs than in Cow Bayou. This is to be expected, as low energy systems such as Cow Bayou allow greater settling time for sorbed or insoluble contaminants and stratification of the water column. Sediment contaminant levels from additional sites in Galveston and Nueces Bays (Table II-10) were higher than those found at Station TB03 (Table 1) for at least one analyte. The single exception was



NB04, another reference site. Several of these sample stations had higher contaminant levels than found at TB02, indicating a high potential for impact to benthic infauna in both Galveston and Nueces Bays.

Benthic macroinvertebrates are often monitored in impact assessments because their populations are indicative of chronic in situ sediment and water quality conditions. Benthos are ecologically important as primary consumers, transferring energy from sediments to higher organisms (Armstrong, 1987). Impacts from produced waters to mobile organisms are much harder to define.

Mackin (1971) found that benthic diversity and abundance was clearly suppressed in Cow Bayou (Harris County, Texas), a bayou dominated by brine, 2500 feet from its confluence with Clear Creek. The highest diversity and abundance of infauna found in Mackin's study was at this confluence. Armstrong et al. (1979) showed a negative correlation between sediment napthalenes concentration and number of species and individuals of benthic fauna near a produced water outfall in Trinity Bay, Texas. He also found that alkane and aromatic hydrocarbons accumulate in sediments up to four times the concentrations found in 100 percent brine effluent and that they persist for least six months after discharge cessation. In a later literature review, Harper (1986) concluded that a "zone of stimulation" or increased production may exceed that lost due to near-field contamination by as much as 10 fold, as more tolerant species increase in abundance in response to reduced competition or an increased carbon source. Apparently, the polychaetes Streblospio benedicti and Polydora ciliata are the most pollution-tolerant and their populations may experience a small increase due to reduced competition.

Previous studies conducted by the Texas Parks and Wildlife Department documented a reduction in shellfish production at sampling stations downstream from brine discharges. Heffernan (1972, 1973) found that white shrimp (Penaeus setiferus), brown shrimp (P. aztecus), and blue crabs (Callinectes sapidus) were less abundant in the Mission River than in other Aransas Bay tributaries with similar hydrological conditions that did not receive brine discharges. Heffernan (1972, 1973) attributes this loss to the effect of petroleum hydrocarbons, yet suggests that the toxic effects from ionic imbalance of brines be further studied. These high salinities are of concern because the concentrations of cations may severely affect aquatic communities for more than one year after termination of discharge (Shipley 1991).

Andreasen and Spears (1983) found that the sheepshead minnow (Cyprinodon variegatus), a tolerant euryhaline species, was severely affected by oilfield brines in toxicity tests. Mackin



(1971) demonstrated that brine (>139 ppt dissolved salts and 19.1 ppm oil) resulted in LC50 values for grass shrimp (P. pugio) and silverside minnows (Menidia beryllina) of 15 and 3 percent effluent, respectively. Differentiation between ionic and hydrocarbon toxicities was not demonstrated.

Analyses of PAH metabolites in striped mullet bile revealed a surprising pattern. Biliary PAH concentrations from Cow Bayou were twice as high as those from Robinson Bayou. In Tabbs Bay metabolites of naphthalene and phenanthrene were more than 10 times background. These results suggest water column or food chain exposure to PAH from uncombusted sources, although their effect are not fully documented. Krahn at al. (1986) and Johnson et al. (1988), documented correlations between PAHs metabolites in bile and reproductive impairment, liver neoplasms and disease in bottom dwelling fishes. Petroleum hydrocarbon residues detected in brown bullheads (Ictalurus nebulosus) were correlated

to the incidence of tumors in the fish (Baumann and Harshbarger 1985). Hickey (personal communication) found that fish communities exposed to PAHs in the environment were skewed toward younger individuals, with the few older fish exhibiting higher tumor rates. Compounds such as aromatic hydrocarbons are thought to become more toxic after metabolic activation in intermediate degradation steps (Varanasi et al. 1985).

King (USFWS, in preparation) studied the effects of brine discharges on shorebirds in Nueces Bay. He color-banded and dyed western sandpipers (Calidris mauri) and short-billed dowitchers (Limnodromus griseus) to demonstrate site fidelity in their winter range. He collected both early-season and late-season (fall and winter) birds for residue analyses and found that sandpipers over-wintering and feeding in the vicinity of brine discharges accumulated significant body burdens of heavy metals and petroleum hydrocarbons.

Impacts to wetland vegetation are the most obvious signs of environmental effect resulting from brine spills or discharges in marsh areas (personal observation) . Emergent marsh plants such as smooth cordgrass (Spartina alterniflora) and gulf cordgrass (Spartina spartinae) are easily killed, even by small volume or intermittent discharges. These "burned" marsh areas are the result of sodium accumulation in soils and may take years to revegetate (Merrill 1990).

Differences in the degree of contamination and biological impacts between tidal bayous and shoreline discharges are evident. As documented in other studies, hydraulic energy is the most important factor governing the fate and effects of these discharges (Harper 1986).

The independent results of benthic community analyses, sediment chemistry analyses, and sediment and pore-water toxicity tests



clearly show that produced water discharges contaminate sediments near them to the extent that infauna are absent or only minimally colonizing them. The most important factor governing the magnitude and extent of contamination or biological impairment caused by any discharge is the degree to which it is mixed into the receiving water body. Discharges to the open Gulf and open bay are better mixed by tidal currents and water depth than discharges to slow-moving bayous and protected shorelines. Bayous and shorelines receive a large proportion of brines discharged in the Galveston Bay system and they are typically more important habitats to fish and wildlife resources. Because of their poor mixing, a greater potential for impact can be expected. Future management of this type of discharge should include a detailed site assessment and recommendations to eliminate or minimize environmental degradation.

Historically the Texas Railroad Commission did not require reporting of actual discharge volumes, water quality parameters other than oil and grease concentration, or exact discharge location, making accurate impact assessments impossible. The TRC is currently updating their permit files and has included

additional reporting and monitoring requirements. In doing so, the TRC now has an accurate estimate of tidal disposal discharges and the volumes discharged into Galveston Bay. Recent estimates of the number of active dischargers, not just permittees, puts the figure at approximately 62 (and a more accurate estimate of 137,000 bbls per day) in the Galveston Bay system. Of the newly estimated 137,000 bbls per day, approximately 80,000 bbls are from one source, which will begin deep-well injection in early 1993.

Although the EPA does not currently regulate these discharges under its NPDES program, they are drafting general NPDES permits for each of the five discharge subcategories. The ones of concern for the Galveston Bay system, the Coastal and stripper subcategories, soon will be issued as a proposed rule, open for public comment. As currently drafted, this proposed rule will require "no discharge" to marshes, wetlands, swamps, bayous or coastal bays from all wells, including stripper wells. The Onshore Subcategory, which has a similar no discharge limitation (except for stripper wells) became a final rule on March 27, 1991.



## LITERATURE CITED

American Society for Testing and Materials (ASTM). 1988. Standard practice for conducting acute toxicity tests with fishes, macroinvertebrates and amphibians. ASTM E 729-88. Philadelphia, PA. pp. 1-19.

American Society for Testing and Materials (ASTM). 1990. Standard guide for conducting solid phase 10-day static sediment toxicity tests with marine and estuarine infaunal amphipods. ASTM E 1367-90, pp. 1-24.

Andreasen, J.K. and R.W. Spears. 1983. Toxicity of Texan petroleum well brine to the sheepshead minnow (C. variegatus) a common estuarine fish. Bull. Environ. Contam. Toxicol. 30:277-283.

Armstrong, H.W., K. Fucik, J.W. Anderson, and J.M. Neff. 1979. Effects of oilfield brine effluent on sediments and benthic organisms in Trinity Bay, TX. Mar. Environ. Res. 2:55-69.

Armstrong, N.E. 1987. The ecology of open-bay bottoms of Texas: a community profile. U.S. Fish Wildl. Serv. Biol. Rep. 98(7.12). 104 pp.

Baker, et al. 1977. A simple hand corer for shallow water sampling, Chesapeake Science, 18 (2), 232-236.

Baumann, P.C. and J.C. Harshbarger. 1985. Frequencies of liver neoplasia in a feral fish population and associated carcinogens. Mar. Environ. Res. 17:324-327.

Boesch, D.F. and N.N. Rabalais (eds). 1989a. Produced waters in sensitive coastal habitats: an analysis of impacts, central coastal Gulf of Mexico. OCS Report/MMS 89-0031, U.S.

Department of the Interior, Minerals Management Service, Gulf of Mexico OCS Regional Office, New Orleans, LA, 157 pp.

Boesch, D.F. and N.N. Rabalais (eds). 1989b. Environmental impact of produced water discharges in coastal Louisiana. Report to the Louisiana Division of the Mid Continent Oil and Gas Association. Louisiana Universities Marine Consortium, Chauvin, LA, 287 pp.

Burch, S. 1991. Unpublished data. U.S. Fish and Wildlife Service, Boise, ID Field Office.



Carr, R.S. and D.C. Chapman. 1992. Comparison of solid-phase and pore-water approaches for assessing the quality of marine and estuarine sediments. Chem. Ecol. (in press).

Carr, R.S. 1991. unpublished data. U.S. Fish and Wildlife Service, National Fisheries Contaminant Research, Corpus Christi, TX.

Chapman, P.M., E.A. Power, R.N. Dexter, and H.B. Andersen. 1991. Evaluation of effects associated with an oil platform using the sediment quality triad. Environ. Toxicol. Chem. 10:407-424.

Hardy, J.T., C.W. Apts, E.A. Crecelius and N.S. Bloom. 1985. Sea-surface microlayer metals enrichment in an urban and rural bay. Est. Cst. Shelf Sci. 20:299-312.

Harper, D.E. 1986. A review and synthesis of unpublished and obscure published literature concerning produced water fate and effects. Galveston, TX: Texas A&M Laboratory. Report to Offshore Operators Committee. 132 pp.

Heffernan, T.L. 1972. The effect of oilfield brine on the Mission River, Aransas Bay area. Texas Parks and Wildlife Department. Coastal Fisheries Project Report. pp. 37-77.

Heffernan, T.L. 1973. Port Bay - An evaluation of the marine habitat. Texas Parks and Wildlife Department. Coastal Fisheries Project Report. pp. 63-91.

Hickey, J. 1990. personal communication. U.S. Fish and Wildlife Service, Cortland, New York Field Office, Gulf Coast Bioassessment Workshop, Port Aransas, TX.

Hose, J.E. 1985. Potential uses of sea urchin embryos for identifying toxic chemicals: description of a bioassay incorporating cytologic, cytogenetic, and embryologic endpoints. J. Appl. Toxicol. 5:245-254.

Howard, C.L. 1991. unpublished data. University of Houston, Clear Lake, TX.

Johnson, L.L., E. Casillas, T. Collier, B.B. McCain, and U. Varanasi. 1988. Contaminant effects on ovarian development in English sole (P. vetulus) from Puget Sound, Washington. Can. J. Fish Aquat. Sci. 45:2133-2146.

King, K. 1991. Manuscript in preparation. U.S. Fish and Wildlife Service, Phoenix, AZ Field Office.

Krahn, M.M., L.D. Rhodes, M.S. Myers, L.K. Moore, W.D. MacLeod, Jr., and D.C. Mains. 1986. Associations between metabolites of aromatic compounds in bile and the occurrence of hepatic



lesions in English sole (P. vetulus) from Puget Sound, Washington. Arch. Environ. Contamin. Toxicol. 15:61-67.

Mackin, J.G. 1971. A study of the effect of oilfield brine effluents on biotic communities in Texas estuaries. Texas A&M Research Foundation project 735 final report to Humble Oil and Refining Company. 72 pp.

Mackin, J.G. 1973. A review of significant papers on effects of oil spills and oil field brine discharges on marine biotic communities. Texas A&M Research Foundation, Proj 737. 104 pp.

McDonald, S. 1991. Manuscript in preparation. Geochemical and Environmental Research Group. Texas A & M University. College Station, TX.

Merrill, S.D., K.J. Lang, and E.C. Doll. 1990. Contamination of soil with oilfield brine and reclamation with calcium chloride. Soil Science 150(1):469-475.

Rabalais, N.N., B.A. McKee, D.J. Reed, and J.A. Means. 1991. Fate and effects of nearshore discharges of OCS produced waters. Volume I: Executive Summary, OCS Study MMS 91-0004, U.S. Department of the Interior, Minerals Management Service, Gulf of Mexico OCS Regional Office, New Orleans, LA. 48 pp.

Rabalais, N.N., B.A. McKee, D.J. Reed, and J.A. Means. 1991. Fate and effects of nearshore discharges of OCS produced waters. Volume II: Technical Report, OCS Study MMS 91-0005, U.S. Department of the Interior, Minerals Management Service, Gulf of Mexico OCS Regional Office, New Orleans, LA. 337 pp.

Rabalais, N.N., B.A. McKee, D.J. Reed, and J.A. Means. 1991. Fate and effects of nearshore discharges of OCS produced waters. Volume III: Appendices, Summary OCS Study MMS 91-0006, U.S. Department of the Interior, Minerals Management Service, Gulf of Mexico OCS Regional Office, New Orleans, LA. 225 pp.

Reid, D. 1983. Radium in formation waters: how much is it of concern? Proceedings 4th Annual Gulf of Mexico Information Transformation Meeting, Mineral Management Service, New Orleans, LA.

SAS Institute Inc. 1988. SAS/STAT User's Guide, Release 6.03 Edition. Cary, NC. 1028 pp.

Shipley, F.S. 1988. Oilfield produced brines in coastal environments: scope of the problem and a case example. Proceedings of the 1988 EPA Water Quality Data Assessment

Workshop. pp. 1-7.



Shipley, F.S. 1991. Oil field-produced brines in a coastal stream: water quality and fish community recovery following long term impacts. The Texas Journal of Science 43(1):51-64.

St. Pe', K.M., ed. 1990. An assessment of produced water impacts to low-energy, brackish water systems in southeast Louisiana. Louisiana Department of Environmental Quality, Water Pollution Control Division, Baton Rouge, Louisiana, 204 pp.

Texas Railroad Commission. 1991. Villamarin, C. personal communication in response to information request.

USEPA and Department of Army Corps of Engineers. 1991. Evaluation of dredged material proposed for ocean disposal (testing manual). EPA 503/8 - 91/001.

USFWS. 1986. Preliminary survey of Contaminant Issues of Concern on National Wildlife Refuges. Dept. of Interior. U.S. Fish and Wildlife Service, Div of Refuge Management. 163 pp.

Varanasi, U., W.L. Reichert, J.E. Stein, D.W. Brown and H.R. Sanborn. 1985. Bioavailability and biotransformation of aromatic hydrocarbons in benthic organisms exposed to sediment from an urban estuary. Environ. Sci. Technol. 19:836-841.



# APPENDIX I - ANALYTICAL METHODS



## METAL ANALYSIS

Samples were lyophilized prior to sample digestion. If necessary, the dried sample was then passed through a 2 mm plastic sieve and a split was then ground using a mortar and pestle. Percent moisture was determined using Standards Methods for the Examination of Water and Wastes, 14th ed. (Section 208A)

Digestions for ICP analysis were performed in accordance with "Procedures for Handling and Chemical Analysis of Sediment and Water Samples", US EPA/COE, Technical Report EPA/CE-81-1, May 1981. One gram aliquots of the dried samples were digested in a vigorous nitric acid-hydrogen peroxide procedure with a final aqueous matrix dilution of 100 mm after filtration. The sample results are reported in mg/kg dry weight. No extraordinary reactions or color changes were noted for the ICP digestion.

Preconcentration of ICP - PH 6: A 30 g sample of the digestate for I.C.P. was weighed into a 50 ml screw top centrifuge tube. One ml of 2000 ppm Indium and 1 ml of 10% ammonium acetate buffer

were added and the pH adjusted to 6.5 with high purity NH[sub]4OH from Seastar. One ml of a 10% DDTC was added and the caps screwed on and mixed by turning end-over-end 6 times slowly. After mixing, the tubes were centrifuged in an I.E.C. refrigerated centrifuge at 20øC for 15 minutes at 15,000 RPM. The liquid was then decanted from the precipitate and 0.3 ml of high purity HNO[sub]3 from Seastar was added. The tubes were heated in a water bath at 95øC to dissolve the precipitate and diluted to 3 ml with deionized water. For samples high in calcium and phosphate a pH of 6.0 was used to reduce the precipitation of Ca[sub]3(PO[sub]4)[sub]2. One sample was spiked and duplicated. Summaries of the ICP QC pages follow:

1. Digestion Blanks - Two blanks were digested with the samples. Normal contamination levels for several analytes were found in the blanks.

2. Initial Calibration Checks - The ICP spectrometer was calibrated properly as indicated by the percent recoveries of the elements analyzed (within ten percent windows) in the initial check solutions.

3. Initial Interference Check - Background correction factors for selected analytes were properly determined as indicated by



percent recoveries for the interference check solutions (within twenty percent windows)

4. Duplicate Analysis - The duplicate precision, as indicated by the Relative Percent Differences (RPD), was acceptable (inside the 20% windows) for all elements with the exception of Al and Pb. Al is only slightly high (21%). The high Pb RPD, at 30%, is probably due to the variability normally found when concentrations are near the IDL.

5. Spike Analysis - Spike recoveries in the sample were within 55 to 120% for most elements. Al, Ba, B, Fe, Mg, and Sr were all low. Low recoveries are typically seen for these elements. As a result, the sample results are probably biased low.

6. Reference Materials - A solid EPA laboratory control sample (0287) was used as a reference material. Recoveries for certified analyte values which could be quantitated at a level above the reporting limit were all within +/- 25% with the exceptions of Ag. Ag recoveries are typically low with this type of digestion.

## AROMATIC AND ALIPHATIC HYDROCARBON ANALYSIS

Sample preparation for the alkanes and aromatics was as follows:

Analysis For Aliphatic and Aromatic Hydrocarbons In Soil and Sediment

Twenty gram soil or sediment samples are extracted with acetone, followed by petroleum ether, by allowing to soak one hour in each with intermittent shaking. A final acetone/petroleum ether

extraction is done, and the extracts are combined, centrifuged, and transferred to a separatory funnel containing sufficient water to facilitate partitioning of residues into petroleum ether portion. The petroleum ether is washed twice with water and concentrated by Kuderna-Danish to appropriate volume for transfer to a 20 gram 1% deactivated silica gel column, topped with five grams neutral alumina. Aliphatic and polynuclear aromatic hydrocarbon residues are fractioned by eluding aliphatics from the column with 100 ml petroleum ether (Fraction I) followed by elution of aromatics using first, 100 ml 40% methylene chloride/60% petroleum ether, then 50 ml methylene chloride (Combined eluates, Fraction II). If needed, Fraction I containing aliphatics is subjected to additional cleanup by concentration and transfer to a deactivated (2% water) Florisil column. Aliphatic residues are eluted from the Florisil column using 200 ml 6% diethyl ether/94% petroleum ether. The eluate is concentrated to appropriate volume for quantification by



capillary column, flame ionization gas chromatography. The silica gel Fraction II containing aromatic hydrocarbons is concentrated, reconstituted in methylene chloride, and subjected to gel permeation chromatographic (GPC) cleanup prior to quantification by capillary, flame ionization gas chemotherapy and fluorescence HPLC.

Analysis For Aliphatic and Polynuclear Aromatic Hydrocarbons and Organochlorine Pesticides in Water

A 500 ml water sample is extracted four times by shaking with 50 ml portions of methylene chloride. The four extracts are combined and concentrated by Kuderna-Danish to near dryness, then reconstituted in 5 ml petroleum ether. An appropriate aliquot is removed for organochlorine and PCB analysis and transferred to a 20 gram Florisil column. The column is eluted with 200 ml 6% diethyl ether/94% petroleum ether (Fraction I) followed by 200 ml 15% diethyl ether/85% petroleum ether (Fraction II). Fraction II is concentrated to appropriate volume for quantification of residues by packed or capillary column electron capture gas chromatography. Fraction I is concentrated and transferred to a silicic acid chromatographic column for additional cleanup required for separation of PCBs from other organochlorines. Three fractions are eluted from the silicic acid column. Each is concentrated to appropriate volume for quantification of residues by packed or megabore column, electron capture gas chromatography. PCBs are found in Fraction II. The remainder of the petroleum ether from the above methylene chloride extraction is transferred to a 20 gram 1% deactivated silica gel column, topped with 5 grams neutral alumina. Aliphatic and polynuclear aromatic hydrocarbon residues are separated by eluting aliphatics from the column with 100 ml petroleum ether (Fraction I) followed by elution of aromatics using first, 100 ml 40% methylene chloride/60% petroleum aromatics ether then. 50 ml methylene chloride (combined eluates, Fraction II). If needed, Fraction I containing aliphatics is subjected to additional cleanup by concentration and transfer to a deactivated (2% water) Florisil column. Aliphatic residues are eluted from the Florisil column using 200 ml 6% diethyl ether/94% petroleum ether. The eluate is

concentrated to appropriate volume for quantification by capillary column, flame ionization gas chromatography. The silica gel Fraction II containing aromatic hydrocarbons is concentrated, reconstituted in methylene chloride, and subjected to gel permeation chromatographic (GPC) cleanup prior to quantification by capillary, flame ionization gas chromatography and fluorescence HPLC.



Analysis For Oil and Grease In Soil and Sediment

Fifty gram soil or sediment samples are extracted with acetone, followed by petroleum ether, by allowing to soak one hour in each with intermittent shaking. The samples are centrifuged, and the supernatant is decanted into a separatory funnel containing sufficient water to facilitate partitioning of residues into petroleum ether portion. Two further acetone/petroleum ether extractions are done, and the extracts are sequentially centrifuged, and transferred to the separatory funnel. The aqueous portion is extracted with petroleum ether and the combined ether extracts are washed twice with water and concentrated by Kuderna-Danish to appropriate volume for transfer. The sample is transferred with petroleum ether rinsing through a bed of sodium sulfate to a tared glass tube. Solvent is removed under nitrogen (N-EVAP), and tube weights are allowed to equilibrate prior to the determination of oil and grease values.

ACID VOLATILE SULFIDES

STANDARDS:

Preparation of Standards:

Primary Standard: The primary S= standard must be prepared fresh every two or three days, due to the instability of N[sub]a2S. To prepare the primary standard, rinse a 50 ml teflon bottle and cap with deionized water, followed by about 5 ml of 4N HCL. Thoroughly rinse the bottle with deionized water making sure there is no trace of acid left in the bottle. Shake any remaining water from the teflon bottle and cap. Add 24 ml of deionized water, 1 ml of 0.08N N[sub]aOH to the teflon bottle. Bubble the water/N[sub]aOH solution for 20 minutes with helium. Quickly weigh out about 6 g of N[sub]a2S 9H[sub]2O into a plastic weighing boat, using a three decimal place balance, and record the weight. Transfer the N[sub]a2S 9H[sub]2O as rapidly as possible to the teflon bottle with the degassed deionized water/N[sub]aOH solution. Do not use this standard until all of the N[sub]a2S has dissolved.

Secondary Standard: The secondary standard must be prepared on a daily basis. To prepare the secondary S= standard, rinse a 100 ml teflon bottle and cap with deionized water, then with about 5 ml of 4N HCL. Thoroughly rinse the bottle with deionized water making sure there is no trace of acid. Shake out any remaining water in the bottle and cap. Add 48 ml of deionized water and 2 ml of 0.08N N[sub]aOH to the teflon bottle. Bubble the water/N[sub]aOH solution for 20 minutes with helium. Add 100 æl of the primary

S= standard to the water/N[sub]aOH solution, cap and mix thoroughly by shaking.

Standard Calculations:

Na[sub]2S 9H[sub]2O fw = 240 g

$$\text{primary standard [S=]æmoles/ml} = \frac{\text{wt(æg) Na[sub]2S 9H[sub]2O}}{\text{Na[sub]2S 9H[sub]2O fw} * \text{vol(ml)}}$$

$$\text{secondary standard [S=]æmoles/ml} = \frac{\text{1ø std [s=]} * .1 \text{ ml}}{50 \text{ ml}}$$

calibration standard [S=] æmoles = 2ø std [S=] * vol(ml) pipetted

The sulfide calibration should consist of a four point standard curve, bracketing the concentrations one expects to see in the samples being analyzed. The 2ø standard concentration can be adjusted to permit one to correctly bracket the sulfide concentrations of interest. Calculate a response factor using linear regression, forcing the line through zero. The analysis is linear to 1.0æmole of S=.

PROCEDURE:

Setup AVS stripping system, with a CaCl[sub]2 drying column, and a liquid N[sub]2 cold trap.

Standards: Add 15 - 20 ml of 4N HCL to the reaction vessel, and bubble with He for 2 minutes, venting the system to the atmosphere. Attach the drying column to the reaction vessel, and the 15% OV-3 on Chromosorb column, immersing the Chromosorb column in liquid N[sub]2. Wait about 30 seconds for the Chromosorb column to cool. Very quickly pipette an aliquot of 2[sub]0 standard into the reaction vessel, and strip for 10 minutes. Disconnect the Chromosorb column from the stripping system, and attach it to the He line for the PID. Place the Chromosorb column in the heater, and press run on the integrator.

SAMPLES:

Aqueous: Thoroughly rinse the reaction vessel and bubbler with deionized water to remove all traces of acid. Place 15 ml of deionized water in the reaction vessel, add .025 - 2 ml of sample, depending on the expected amount of AVS in the sample, and bubble for 2 minutes, venting the system to the atmosphere. Attach the CaCl[sub]2 drying column to the system. Place the Chromosorb column in-line with the stripping system, and immerse the column in liquid N[sub]2. Add 4 ml of 4N HCL to the reaction vessel through the He inlet port, and strip for 10 minutes. Put



the Chromosorb column in-line with the PID, (photo ionization

detector), place the column in the heater, and press run on the integrator. Thoroughly rinse the reaction vessel and the bubbler. Start another sample.

Sediment: Thoroughly rinse the reaction vessel and bubbler with deionized water to remove all traces of acid. Remove the top 2-3 mm of sediment from the sample container and discard. Mix the sample thoroughly with a teflon spatula and recap the sample container. Record the sample ID number of a S= sheet. Weigh the sample container to 3 decimal places, and record the weight. Record the sample ID number on a weighing tin, and weigh the empty tin, recording the weight. Tare the balance with the weighing tin, weigh out about 1-3g of sediment with a clean teflon spatula, for moisture determination, and place .01 - .1g of sediment in the reaction vessel, making sure to get all of the sediment off the spatula. Bubble the sediment sample for 2 minutes with He, venting to the atmosphere. Record the weight of the weighing tin and sediment, and reweigh the sample bottle, recording its weight. Place the weighing tin and sediment in the drying oven. Attach the CaCl[sup]2 drying column to the reaction vessel, immerse the Chromosorb column in liquid Ný and attach to the drying column. Wait 30 seconds to allow the column to cool, add 4 ml of 4N HCl to the reaction vessel through the He inlet port, and bubble for 10 minutes. Place the Chromosorb column in-line with the PID, press run on the integrator, and record the peak area. Rinse the reaction vessel, and start another sample.

Calculations:

$$\%dry = \frac{\text{sam wt (wet)} - \text{sam wt (dry)}}{\text{sam wt (wet)}} * 100$$

[S=]æmoles = peak area * response factor

$$[S=]\text{æmoles/g(dry)(or vol)} = \frac{[S=]\text{æmoles}}{\text{sam wt g(dry) (or vol)}}$$

Instrumentation:
_____stripper flow rate: 120 ml/min
PID flow rate: 70 ml/min
oven temp: 50øC.

% Moisture: For animal tissue and sediments of sufficient size, moisture was determined by placing a weighed aliquot of the sample in a Fisher Isotemp oven and drying at 103-105øC. The dried sample was then weighed and the data entered into a computer program to generate the % moisture and final report.



Homogenization: For sediments, the sample was mixed and an aliquot weighed and frozen. The frozen samples were placed in a Labcono Freeze Dryer 8 until the moisture has been removed. The dry samples were then weighed and further homogenized using a

blender, or Spex Industries, Inc. Model 8000 mixer/mill with tungsten-carbide vial and balls.

The Analysis of Aromatic Hydrocarbon Metabolites in Bile: Bile samples are analyzed for naphthalene, phenanthrene, and benxo[a]pyrene metabolites by an HPLC-fluorescence detection method. Samples are injected directly into an HPLC. Detector response is monitored at 292/335 (naphthalene), at 257/380 (phenanthrene), and at 380/430 (benzo[a]pyrene) EX/FM wavelength pairs.

The QA/QC for these samples include analyzing appropriate standards and reagent blanks for each run. During a sample run, a calibration check is analyzed after every sixth sample. Additionally, each run includes a minimum of 10% duplicate sample analyses. Calibration checks and duplicates have an RSD of 10% or less. Additionally, a reference bile sample is analyzed with each sample run and must agree within +/- 15% of the previous reference bile run and has an overall RSD that is no greater than +/- 20%.

Radium Analyses - Neutron activation

Water - (Radioactivity Analysis) The measurement of total radium alpha emitters in surface and ground water is achieved using EPA SW-846 Method 9315. Alpha emitters having energies above 3.9 Mega Electron Volts (MeV) are detected with this method.

Method Summary

Radium isotopes from one liter of sample are co-precipitated on barium and lead sulfate. After settling, the liquid is decanted off and the remaining solids are then centrifuged and dissolved in EDTA solution. The barium sulfate is reprecipitated, centrifuged, and transferred to a counting planchet. The sample is then dried using an IR lamp and counted on a low background alpha/beta counter for one hour. All counts are corrected for the milligram loading of residue on the counting planchet due to dissolved solids in the sample and ingrowth of radium daughter products. The results of these analyses are reported in pCi/L with the Method Blank activity subtracted.

Specific Details

EPA Method 9315 calls for the analysis of 1000 ml of sample. In all instances where less than this volume of sample was



submitted, smaller volumes were analyzed. The uncertainty of all analyses is reported to two sigma, which is defined as two times the square root of the number of counts over the number of counts. NIST SRM 4957 Ra-226 was used for all sample spike QC.

Soil - (Neutron activation Analysis) Alpha and Gamma Spectroscopy.

# APPENDIX II - SUMMARY TABLES



Table II-1. Analyses conducted by U.S. Fish and Wildlife Service contract laboratories.

| | | Petroleum Hydrocarbons | |
|---|---|---|---|
| Heavy Metals | Non-Routine Analyses | Aliphatics | Aromatics |
| Aluminum | total organic carbon | n - dodecane | PAH1 - napthalene |
| Arsenic | radium | n - tridecane | PAH2 - fluorene |
| Boron | acid volatile solids | n - tetradecane | PAH3 - phenanthrene |
| Barium | grain size | n - pentadecane | PAH4 - anthracene |
| Beryllium | percent moisture | n - hexadecane | PAH5 - fluoranthrene |
| Cadmium | | n - heptadecane | PAH6 - pyrene |
| Chromium | | n - octadecane | PAH7 - 1,2-benzanthracene |
| Copper | | n - nonadecane | PAH8 - chrysene |
| Iron | | n - eicosane | PAH9 - benzo(b)fluroanthrene |
| Lead | | nonylcyclohexane | PAH10- benzo(k) fluoranthrene |
| Magnesium | | octylcyclohexane | PAH11- benzo(e)pyrene |
| Manganese | | phytane | PAH12- benzo(a)pyrene |
| Mercury | | pristane | PAH13- 1,2,5,6-dibenzanthracene |
| Molybdenum | | | PAH14- benzo(g,h,i)perylene |
| Nickel | | | |
| Selenium | | | |
| Silver | | | |
| Strontium | | | |
| Thallium | | | |
| Vanadium | | | |
| Zinc | | | |

Table II-2. Reporting units and detection limits for all analyses.

| Parameter | Matrix | Unit | Detection |
|---|---|---|---|
| PAH | Sediment | ppm - wet wt | 0.01 |
| | Water | ppm - wet wt | 0.005 |
| | Tissue | ppm - wet wt | 0.01 |
| Aliphatics | Sediment | ppm - wet wt | 0.010 |
| | Water | ppm wet wt | 0.005 |
| | Tissue | ppm - wet wt | 0.010 |
| Oil & Grease | Sediment | ppm - wet wt | 10.000 |

| | | | |
|---|---|---|---|
| | Water | ppm | 10.000 |
| AVS | Sediment | æmoles/g dry wt | Variable |
| TOC | Sediment | % dry wt | 0.100 |
| Grain Size | Sediment | % dry wt | 0.100 |
| Radium | Sediment | Picocuries Ra/g soil | Variable |
| | Water | Picocuries Ra/1 | Variable |

| Metals | Water mcg/ml | Sediment mg/kg dry wt |
|---|---|---|
| Silver | NA | 2.0 |
| Aluminum | .007 | 3.0 |
| Arsenic | NA | 20.0 |
| Boron | NA | 2.0 |
| Barium | NA | 0.1 |
| Beryllium | .000 | 0.1 |
| cadmium | .000 | 1.0 |
| chromium | .003 | 1.0 |
| copper | .0007 | 0.5 |
| Iron | .020 | 10.0 |
| Magnesium | NA | 4.0 |
| Manganese | .0005 | 0.3 |
| Molybdenum | NA | 1.0 |
| Nickel | .005 | 2.0 |
| Lead | .009 | 6.0 |
| Selenium | NA | 10.0 |
| Strontium | NA | 0.1 |
| Thallium | .010 | 5.0 |
| Vanadium | NA | 0.5 |
| Zinc | .001 | 0.6 |



Table II-3. Summary of bioassays conducted in this study.

| Species | Test Type | Endpoint | Duration |
|---|---|---|---|
| Arbacia | Pore-water | Morphological development | 48h |
| Arabacia | Pore-water | Fertilization | 1h |
| Grandidierella | solid-phase | Survival | 48h |
| Hyalella | solid-phase | Survival | 28d |
| Palaemonetes | solid-phase | Survival | 10d |
| Palaemonetes | Resuspended solids | Survival | 96h |
| sciaenops | Pore-water | Hatching success | 96h |

| | | | |
|---|---|---|---|
| Sciaenops | Pore-water | Survival | 96h |
| Sciaenops | Microlayer | Survival | 96h |
| Sciaenops | Subsurface | Survival | 96h |
| Sciaenops | Effluent | Survival | 96h |

Table II-4. äPAHs, äaliphatics, oil and grease, and total organic carbon in sediments.

| Station | äPAH[sup]1 | äALI[sup]1 | OIL[sup]1 | TOCý |
|---|---|---|---|---|
| ANWR | 0.15 | 3.860 | 1110 | 1.6 |
| BLPT | 0.02 | 22.040 | 622 | 0.3 |
| C1SE | 0.31 | 0.400 | 522 | 1.2 |
| C2SE | 2.70 | 12.220 | 1370 | 1.3 |
| CB01 | 3.05 | 1.410 | 1390 | 1.1 |
| CB02 | 2.92 | 4.580 | 1760 | 1.3 |
| CB03 | 2.17 | 2.245 | 1070 | 0.7 |
| CB04 | 0.35 | 0.330 | 350 | 1.2 |
| EX1 | 1.75 | 93.700 | 8170 | 1.9 |
| EX3 | 7.97 | 457.000 | 55900 | 11.0 |
| GBR | 0.03 | 0.210 | 290 | 0.5 |
| HI2 | 1.02 | 1.700 | 830 | 1.4 |
| HI3 | 0.04 | 1.200 | 1120 | 1.6 |
| NB01 | 0.43 | 10.500 | 850 | 0.9 |
| NB02 | 0.28 | 5.800 | 952 | 0.4 |
| NB03 | 7.94 | 1.800 | 436 | 0.2 |
| NB04 | 0.00 | 0.040 | 96 | 0.2 |
| RB01 | 0.21 | 0.230 | 538 | 1.4 |
| RB02 | 0.21 | 0.240 | 554 | 1.0 |
| TB01 | 0.35 | 4.810 | 1930 | 0.2 |
| TB02 | 0.36 | 6.940 | 3630 | 1.1 |
| TB03 | 0.26 | 0.710 | 686 | 1.1 |
| TB04 | 0.26 | 0.600 | 566 | 1.1 |
| TB05 | 0.34 | 1.200 | 814 | 0.9 |
| TB06 | 0.53 | 0.980 | 762 | 1.2 |
| TB07 | 0.21 | 0.810 | 810 | 1.0 |
| TB08 | 0.15 | 0.450 | 620 | 0.8 |
| TB09 | 0.08 | 0.320 | 422 | 0.7 |
| TB11 | 0.29 | 1.430 | 1150 | 0.3 |
| TB12 | 0.01 | 0.230 | 240 | 0.1 |

[sup]1 ppm wet weight

ýpercent dry weight



Table II-5. Results of ICP scan for trace metals in sediments (mg/kg dry weight).

See Table/Figure

Table II-6. Estimated distance from discharge to sample station.

| Station | Distance (feet) |
|---|---|
| TB01 | 90 |
| TB02 | 270 |
| TB03 | 1,200 |
| TB04 | 3,300 |
| TB05 | 1,200 |
| TB06 | 3,300 |
| TB07 | 1,200 |
| TB08 | 3,300 |
| TB09 | 9,000 |
| TB11 | 450 |
| TB12 | 450 |
| GBR | 7,040 |
| CB01 | 3,310 |
| CB02 | 6,640 |
| CB03 | 7,510 |
| CB04 | 8,510 |
| RB01 | 14,510 |
| RB02 | 15,840 |



Table II-7. Grain size(%), acid volatile sulfides(æm/g), total organic carbon(%), and moisture(%) in sediment samples.

| STA | SAND | SILT | CLAY | AVS | TOC | MOI |
|---|---|---|---|---|---|---|
| ANWR | 41.2 | 47.7 | 11.1 | 0.0 | 1.6 | 18.8 |
| BLPT | 56.9 | 26.2 | 16.9 | 12.5 | 0.3 | 34.0 |
| C1SE | 23.4 | 43.9 | 32.7 | 6.6 | 1.2 | 47.8 |
| C2SE | 18.0 | 29.6 | 52.4 | 48.5 | 1.3 | 63.8 |
| CB01 | 19.6 | 41.8 | 38.6 | 22.0 | 1.1 | 52.2 |
| CB02 | 16.6 | 43.1 | 40.3 | 55.2 | 1.3 | 52.4 |
| CB03 | 38.5 | 30.0 | 31.5 | 46.2 | 0.7 | 47.6 |
| CB04 | 18.2 | 33.9 | 47.9 | 13.8 | 1.2 | 57.2 |
| EX1 | 38.7 | 41.1 | 20.1 | 25.9 | 1.9 | 50.0 |
| EX3 | 9.6 | 60.8 | 29.5 | 4.3 | 11.0 | 73.6 |
| GBR | 53.5 | 21.0 | 25.6 | 3.2 | 0.5 | 42.0 |
| HI2 | 26.6 | 40.1 | 33.3 | 22.9 | 1.4 | 49.2 |
| HI3 | 21.9 | 41.9 | 36.2 | 37.0 | 1.6 | 56.4 |
| NB01 | 39.4 | 26.9 | 33.7 | 15.9 | 0.9 | 46.6 |
| NB02 | 70.9 | 14.1 | 15.0 | 3.5 | 0.4 | 31.0 |
| NB03 | 86.4 | 6.2 | 7.4 | 0.0 | 0.2 | 30.8 |
| NB04 | 90.5 | 3.1 | 6.4 | 2.1 | 0.2 | 23.4 |
| RB01 | 12.5 | 36.9 | 50.5 | 31.9 | 1.4 | 62.8 |
| RB02 | 16.6 | 38.4 | 45.0 | 20.8 | 1.0 | 56.4 |
| TB01 | 84.3 | 9.8 | 5.9 | 14.2 | 0.2 | 24.2 |
| TB02 | 18.5 | 41.9 | 39.6 | 48.7 | 1.1 | 53.2 |
| TB03 | 2.5 | 41.0 | 56.5 | 61.7 | 1.1 | 63.0 |
| TB04 | 27.5 | 30.2 | 42.2 | 19.2 | 1.1 | 53.6 |
| TB05 | 4.4 | 46.7 | 48.9 | 18.4 | 0.9 | 50.2 |
| TB06 | 10.1 | 38.1 | 51.8 | 13.2 | 1.2 | 61.2 |
| TB07 | 3.5 | 48.0 | 48.5 | 17.5 | 1.0 | 51.6 |

| | | | | | | |
|---|---|---|---|---|---|---|
| TB08 | 16.4 | 42.2 | 41.4 | 28.8 | 0.8 | 46.6 |
| TB09 | 22.6 | 41.8 | 35.6 | 8.0 | 0.7 | 51.6 |
| TB11 | 87.9 | 6.3 | 5.8 | 1.1 | 0.3 | 23.0 |
| TB12 | 91.9 | 4.8 | 3.3 | 1.4 | 0.1 | 24.8 |

Table II-8. Benthic community data from the Cow Bayou and Tabbs Bay study site.

| station | statistic | abundance | richness | diversity |
|---|---|---|---|---|
| CB01 | $\bar{x}$ | 0.00 | 0.00 | 0.00 |
| | n | 7.00 | 7.00 | 7.00 |
| | s.d. | 0.00 | 0.00 | 0.00 |
| CB02 | $\bar{x}$ | 5.14 | 0.86 | 0.14 |
| | n | 7.00 | 7.00 | 7.00 |
| | s.d. | 5.21 | 1.07 | 0.36 |
| CB03 | $\bar{x}$ | 9.43 | 1.57 | 0.37 |
| | n | 7.00 | 7.00 | 7.00 |
| | s.d. | 10.10 | 0.98 | 0.36 |
| CB04d | $\bar{x}$ | 13.00 | 2.60 | 0.60 |
| | n | 5.00 | 5.00 | 5.00 |
| | s.d. | 9.75 | 0.89 | 0.36 |
| CB04u | $\bar{x}$ | 10.80 | 3.80 | 1.11 |
| | n | 5.00 | 5.00 | 5.00 |
| | s.d. | 4.02 | 1.10 | 0.27 |
| RB01 | $\bar{x}$ | 28.00 | 4.00 | 1.05 |
| | n | 5.00 | 5.00 | 5.00 |
| | s.d. | 19.00 | 2.00 | 0.30 |
| RB02 | $\bar{x}$ | 30.00 | 6.40 | 1.43 |
| | n | 5.00 | 5.00 | 5.00 |
| | s.d. | 18.70 | 1.14 | 0.28 |
| TB01 | $\bar{x}$ | 1.57 | 1.00 | 0.08 |
| | n | 7.00 | 7.00 | 7.00 |
| | s.d. | 1.40 | 0.58 | 0.21 |
| TB02 | $\bar{x}$ | 4.29 | 2.00 | 0.56 |
| | n | 7.00 | 7.00 | 7.00 |
| | s.d. | 2.69 | 0.82 | 0.43 |
| TB03 | $\bar{x}$ | 18.20 | 4.63 | 1.03 |
| | n | 5.00 | 5.00 | 5.00 |
| | s.d. | 7.12 | 1.21 | 0.30 |
| TB04 | $\bar{x}$ | 23.00 | 4.28 | 1.06 |
| | n | 7.00 | 7.00 | 7.00 |
| | s.d. | 18.10 | 1.81 | 0.48 |
| TB05 | $\bar{x}$ | 32.10 | 4.86 | 1.26 |
| | n | 7.00 | 7.00 | 7.00 |
| | s.d. | 24.10 | 1.07 | 0.19 |
| | $\bar{x}$ | | | |

| | | | | |
|---|---|---|---|---|
| TB06 | x | 18.30 | 5.43 | 1.45 |
| | n | 7.00 | 7.00 | 7.00 |
| | s.d. | 6.32 | 0.98 | 0.17 |
| TB07 | $\bar{x}$ | 24.40 | 5.71 | 1.39 |
| | n | 7.00 | 7.00 | 7.00 |
| | s.d. | 9.68 | 1.25 | 0.23 |
| TB08 | $\bar{x}$ | 23.10 | 4.57 | 1.23 |
| | n | 7.00 | 7.00 | 7.00 |
| | s.d. | 17.20 | 1.51 | 0.32 |

(Continued)



Table II-8. (Concluded)

| station | statistic | abundance | richness | diversity |
|---|---|---|---|---|
| TB09 | $\bar{x}$ | 23.10 | 4.86 | 1.31 |
| | n | 7.00 | 7.00 | 7.00 |
| | s.d. | 13.70 | 0.90 | 0.21 |
| TB11 | $\bar{x}$ | 30.80 | 5.40 | 1.32 |
| | n | 5.00 | 5.00 | 5.00 |
| | s.d. | 13.50 | 0.89 | 0.18 |
| TB12 | $\bar{x}$ | 12.80 | 3.60 | 0.73 |
| | n | 5.00 | 5.00 | 5.00 |
| | s.d. | 8.14 | 1.67 | 0.55 |
| TBR1 | $\bar{x}$ | 15.10 | 4.00 | 1.10 |
| | n | 7.00 | 7.00 | 7.00 |
| | s.d. | 9.10 | 2.38 | 0.59 |



Table II-9. Radium-226 in sediments, water, and effluent samples.

| Station | water | std. dev. | sediment | std. dev. |
|---|---|---|---|---|
| ANWR | <10.00 | | 0.310 | 20.0 |
| BLPT | NA | | 5.137 | 8.0 |
| C1SE | NA | | 2.003 | 12.5 |
| C2SE | 2.17 | 0.72 | 3.643 | 10.0 |
| CB01 | NA | | 1.224 | 15.0 |
| CB02 | 3.81 | 1.90 | 0.621 | 20.0 |
| CB03 | 10.07 | 2.74 | 1.935 | 12.5 |
| CB04 | 1.49 | 0.58 | 2.768 | 12.5 |
| EX1 | NA | | 1.386 | 15.0 |
| EX1-effluent | 125.56 | 9.63 | | |
| EX3 | NA | | 4.036 | 10.0 |
| GBR | <0.50 | | 0.980 | 17.5 |
| HI2 | 4.27 | 1.32 | 1.900 | 12.5 |
| HI2 | <10.00 | | | |

| | | | | |
|---|---|---|---|---|
| HI3 | NA | | 1.460 | 15.0 |
| NB01 | <50.00 | | 1.233 | 15.0 |
| NB01-effluent | <10.00 | | | |
| NB02 | 2.32 | 0.70 | 1.371 | 15.0 |
| NB02-effluent | <10.00 | | | |
| NB03 | NA | | 1.273 | 15.0 |
| NB03-effluent | <10.00 | | | |
| NB04 | NA | | 0.442 | 20.0 |
| RB01 | 1.23 | 0.57 | 2.047 | 12.5 |
| RB02 | 4.51 | 1.77 | 1.066 | 15.0 |
| TB01 | 1.47 | 0.57 | 1.452 | 15.0 |
| TB01-effluent | 128.74 | 14.09 | | |
| TB01-pore water | 18.39 | 4.28 | | |
| TB02 | <0.50 | | 2.620 | 12.5 |
| TB03 | <0.50 | | 1.615 | 12.5 |
| TB04 | <0.50 | | 1.090 | 15.0 |
| TB05 | <0.50 | | 3.179 | 10.0 |
| TB06 | 0.89 | 0.53 | 3.455 | 10.0 |
| TB07 | 3.38 | 1.11 | 3.870 | 10.0 |
| TB08 | <0.50 | | 2.079 | 12.5 |
| TB09 | <0.50 | | 1.175 | 15.0 |
| TB11 | 1.23 | 0.52 | 0.764 | 17.5 |
| TB12 | 2.52 | 1.59 | 1.335 | 15.0 |



Table II-10. Locations of additional sample stations.

| Station | Location | County |
|---|---|---|
| ANWR | Anahuac National Wildlife Refuge | Chambers |
| BLPT | Black Point, Trinity Bay shoreline | Chambers |
| C1SE | C1 separator, Trinity Bay | Chambers |
| C2SE | C2 separator, Trinity Bay | Chambers |
| EX1 | ditch along Hwy. 3 near Pineloch | Harris |
| EX3 | ditch along Hwy. 3, near El Dorado Blvd. | Harris |
| HI2 | tidal bayou, adjacent to GIWW, 10,600 feet east of the High Island Bridge | Galveston |
| HI3 | East Bay Bayou, 8,000 feet east of the High Island Bridge (2,600' NW of HI2) | Galveston |
| NB01 | White's Point, Nueces Bay | Nueces |
| NB02 | White's Point, Nueces Bay | Nueces |
| NB03 | White's Point, Nueces Bay | Nueces |
| NB04 | Aransas Bay (Reference) | Aransas |

Table II-11. Specific aromatic hydrocarbons detected in sediments.

See Table/Figure

Table II-12 Benthic organisms collected during this study, by taxa.

See Table/Figure

Table II-12. Continued.

See Table/Figure



Table II-12. Concluded.

See Table/Figure

Table II-13. Benthic infauna identified in Galveston Bay sediments

| Code Number | Lowest taxa identified |
|---|---|
| SP40 | Rhynchocoela |
| SP50 | Nematoda |
| | Annelida:Polychaeta |
| SP61 | Mediomastus californiensis |
| SP62 | Capitella capitata |
| SP63 | Streblospio benedicti |
| SP65 | Neanthes succinea |
| SP66 | Polydora ligni |
| SP70 | Annelida:Oligochaeta |
| | Mollusca:Bivalvia |
| | Rangia cuneata |
| SP82 | Macoma mitchilli |
| SP90 | Mollusca: Gastropoda |
| | Arthropoda:Crustacea:Copepoda:Cyclopoida |
| SP111 | Acartia tonsa |
| SP120 | Arthropoda:Crustacea:copepoda:Cyclopoida |
| | Arthropoda:Crustacea:copepoda:Harpacticoida |
| SP131 | Scottolana canadensis |
| SP140 | Arthropoda:Crustacea:Ostracoda |
| | Arthropoda:crustacea:Isopoda |
| SP151 | Edotea triloba |
| | Arthropoda:crustacea:Amphipoda |
| SP162 | Erichthonius brasiliensis |